SOAP CONTROL AGENT

This invention relates to phosphonated polymers as naphthenate and carboxylate salt control agents, the use of such agents and the method of use of such agents.

Crude oil invariably contains naphthenic and carboxylic/fatty acids in varying amounts dependent upon the source of the crude oil.

When crude oil contacts an aqueous phase, for example reservoir water, it is possible for metal salts of naphthenic and fatty acids to be formed. The metal ions in the aqueous phase can react with carboxylic groups on the acids to form salts (these are typically referred to as soaps).

These soaps can be very problematic during oil recovery and downstream processing. Typical problems include:

- the formation of oil water sludge and emulsions which hinder oil water separation processes;

- the formation of hard or waxy scales which cause retardation of fluid flow, block processing equipment and reduce the quality of the oil;

- soluble metal soaps remaining in the crude oil during the separation process and accordingly the crude oil contains residual levels of metal ions such as calcium, magnesium and iron;

- the presence of metal ions reducing the value of the crude oil; and

- the presence of metal ions also causing processing problems as soaps can deposit in preheat trains and decompose during resid conversion, hydroconversion or coking procedures.

Currently, naphthenate and carboxylate soap formation is treated by the addition of large volumes of acids such as acetic acid. However, this type of treatment suffers from volumes of acetic acid being needed and high corrosion rates that are experienced as a result of using acetic acid.

The present invention aims to ameliorate the above disadvantages by providing a non-corrosive treatment that can effectively control naphthenate and carboxylate soap formation during oil recovery and processing operations.

Accordingly, the present invention provides a soap control agent comprising a phosphorus containing polymer.

Further provided is the use of a phosphorus containing polymer, as a soap control agent, to control soap formation.

Also provided is the use of a phosphorus containing polymer in the manufacture of an agent to control soap formation.

The phosphorus containing polymer may have a phosphonate or phosphinate end cap. The end capped polymer may be of formula (I):

$X_2O_3PCHYCZ_2PO_2XR$ (I)

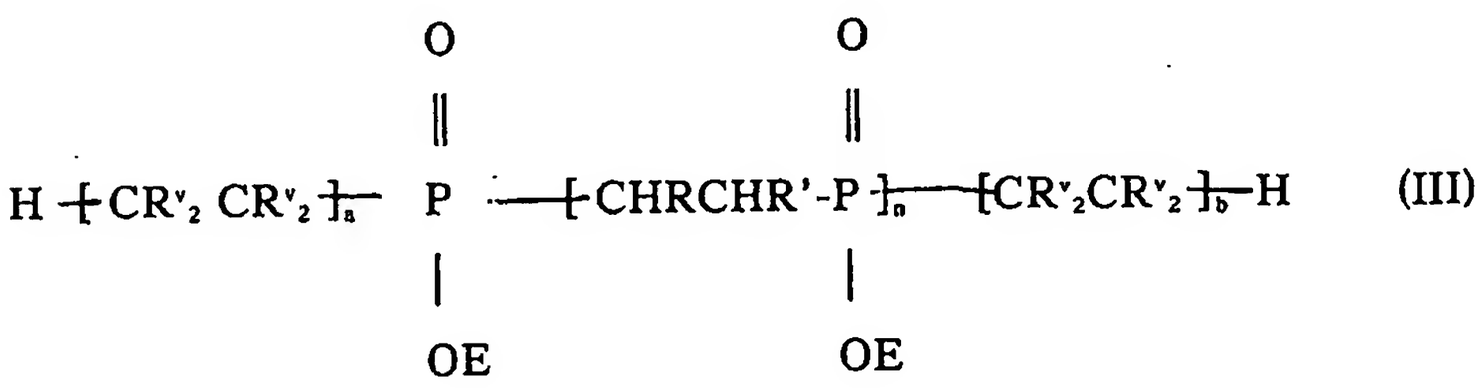
wherein X is H or an alkali metal, alkaline earth or other polyvalent metal, ammonium or an organic base, and R is a polymeric chain comprising between 1 and 100,000 groups, said group or groups being

derived from at least 1 unsaturated compound in which the multiple bond is activated chemically by an adjacent electron withdrawing group, and Y and Z are each hydrogen, a PO_3A_2, SO_3A or CO_2A group wherein A is hydrogen or an alkyl or aryl moiety.

R is preferably a polymer of acrylic acid. Alternatively, R is a polymer of a carboxylic or sulphonic acid, e.g. methacrylic acid, maleic acid, vinyl sulphonic acid or 2-acrylamido-2-methylpropane sulphonic acid. R may also be a copolymer of VPA (vinyl phosphonic acid) and VDPA (vinyl diphosphonic acid).

The compound may exist either as a free acid or as its salt. The compounds are normally prepared and used in the form of water soluble salts. The compounds of formula (I) and methods for preparing them are set out in detail in European Patent No 0 861 846 of Rhodia Consumer Specialties Limited.

Alternatively, the phosphorus containing polymer may be a telomer of formula (III):



(III)

wherein E is hydrogen or a cation, R and R' are each independently selected from the group consisting of hydrogen, hydroxyl, carboxyl, alkyl, aryl, alkaryl, hydroxy-substituted alkyl, aryl or alkaryl and carboxy-substituted alkyl, aryl or alkaryl, provided that R and R' together have a total of less than 23 carbon atoms,

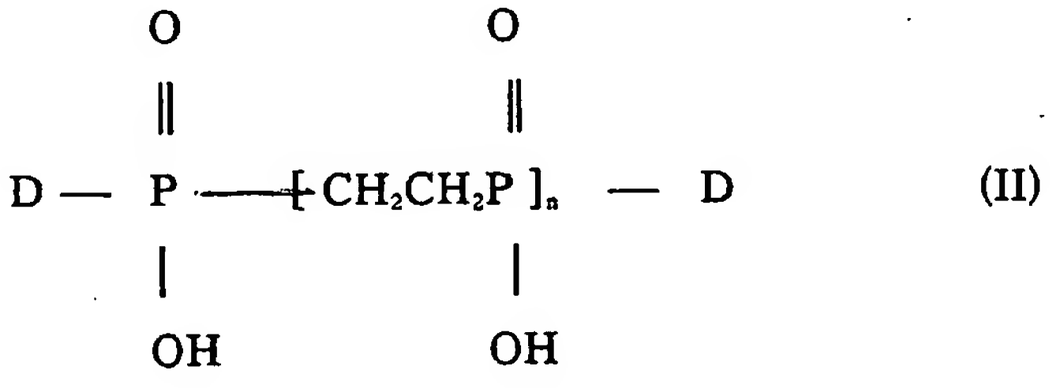
at least one R^v in each monomer unit is selected from the group consisting of hydroxy, carboxy, sulpho, phosphono, amido, aceto, aryl and halogen;

each other R^v is independently selected from the group consisting of hydrogen, C_{1-4} alkyl, carboxyl, sulpho, phosphono, hydroxyl groups, carboxy-substituted, sulpho-substituted, phosphono-substituted and hydroxy-substituted C_{1-4} alkyl groups;

(a+b) is in the range 5 to 200 and n is greater than 1.

The telomer of formula (III) is preferably produced by co-polymerising a polymer of formula II (below) with at least one monomer of formula $CR_2^v=CR_2^v$, wherein R^v has the same meaning as above.

Formula (II) is:



(II)

wherein D is hydrogen or a cation or an alkyl group and n is 1.05 to 100.

The present invention, in a further aspect, provides the use of a soap control agent as defined above to either remove metal ions from a medium or to inhibit the formation of problematic metal soaps.

The medium is preferably crude oil. Alternatively, the medium is a mixture, in any proportion, of hydrocarbons containing naphthenic or fatty acids with water. In particular, the water can be injection water, reservoir water (connate water) or water from oil fields, or any system

where water contact or is in contact with crude oil or naphthenic acid or fatty acid containing fluids.

Furthermore, the medium can be selected from processed soaps and cleaning formulations as used in personal home care applications.

The present invention in a yet further aspect, provides a method of removing metal ions from a medium comprising contacting the medium with an effective amount of a phosphorus containing polymer as described above.

The medium is preferably crude oil. Alternatively, the medium is a mixture, in any proportion, of hydrocarbons containing naphthenic or fatty acids with water. In particular, the water can be injection water, reservoir (connate water) or produced water from oil fields, or any system water or in contact with crude oil or naphthenic acid or fatty acid containing fluids. Furthermore, the medium can be processed soaps and cleaning formulations as used in personal homecare applications.

The soap control agent is used in an effective amount of between 0.01 to 100,000ppm. Preferably the soap control agent is used in an effective amount of between 1 to 10,000ppm.

The soap is preferably selected from the group consisting of calcium naphthenate, sodium naphthenate, magnesium naphthenate, iron naphthenate, calcium carboxylate, magnesium carboxylate and iron carboxylate.

The metal ions are preferably selected from the group consisting of:
Mg^{2+}, Ca^{2+}, Na^{+}, Fe^{2+}/Fe^{3+}.

It will be appreciated that the use of the soap control agent according to the invention is not to be limited to soap control in crude oil. The soap control agent may be used in other areas where soap control is important, for example, laundry detergents and domestic cleaning products.

It is believed that the soap control agents work by sequestering metal ions. Once the metal ions have been sequestered, soap formation is inhibited. It is also believed that the polymers in accordance with the invention interact with soaps to destabilise them. This is, of course, a theory and should not be construed as being limiting or factual.

It is advantageous that the use of phosphonated polymers in accordance with the present invention controls soap formation with no emulsification of the oil-water systems.

The present invention will now be described, with reference to the following example.

Example 1

Potential soap control agents were added to 70mls of a crude oil, previously characterised as containing 50ppm Ca, at a treatment level of 500ppm product. The treated crude oil was stored at 60°C for 2 hours. The crude oil was washed with 30mls of de-ionised water to remove any water-soluble calcium compounds from the oil. The "washing" was processed to remove residual oil. The processed washings were then analysed for calcium content using ICPES (inductively coupled plasma emission spectroscopy).

Effective soap control agents will scavenge the calcium from the crude oil and migrate into the de-ionised water. Therefore, the efficacy of the soap

control agent is directly proportional to the amount of calcium in the processed washings.

The results are summarised below:

Soap control agent evaluated Evaluated	ppm Calcium in deionised water after extraction
Control (de-ionised water)	14
Long chain mono-phosphonic acid	2
Oil soluble phosphonocarboxylate	5
HEDP – conventional phosphonate	6
Long chain di-phosphonic acid	6
Dialkyl alkyl phosphonate	11
Short chain phosphonocarboxylate	21
Phosphonate end capped polymer I	57
Short chain phosphine oxide	29
Acetic acid	32
P-Block polymer	60
Phosphonate end capped polymer II	61

This table shows that the novel phosphorus containing compounds (phosphonate end capped polymer I, P-block polymer and phosphonate end capped polymer II), in accordance with the invention, effectively decrease the amount of metal ions in crude oil and thereby inhibit soap formation and alleviate the problems associated with soaps in crude oil.